



## UV photolysis of quinoline in interstellar ice analogs

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**Abstract**–The polycyclic aromatic nitrogen heterocycle (PANH) quinoline ( $C_9H_7N$ ) was frozen at 20 K in interstellar ice analogs containing either pure water or water mixed with methanol or methane and exposed to ultraviolet (UV) radiation. Upon warming, the photolysis products were analyzed by high-performance liquid chromatography and nanoscale liquid chromatography-electrospray ionization mass spectrometry.

A suite of hydroxyquinolines, which were formed by the addition of oxygen atoms to quinoline, was observed as the primary product in all the ices. Quinoline N oxide was not formed, but five hydroxyquinoline isomers were produced with no clear dominance of one isomer. Reduction products, formed by hydrogen atom addition, were also created. Ices created at 20 K with  $H_2O$ :quinoline ratios of 10:1 to 100:1 showed similar product distributions to those at 122 K, with no apparent temperature or concentration dependence. Increasing the UV dose led to a decrease in overall yield, indicating that quinoline and its products may be photo-destroyed.

Methylquinolines were formed upon photolysis of the methanol- and methane-containing ices. In addition, possible methoxyquinolines or quinoline methylene alcohols were formed in the methanol-containing ice, while methylhydroxyquinolines were created in the methane-containing ice.

This work indicates that oxidation of PANHs could occur in icy extraterrestrial environments and suggests that a search for such compounds in carbonaceous meteorites could illuminate the possible link between interstellar ice chemistry and meteoritic organics. Given the importance of oxidized and alkylated PANHs to biochemistry, the formation and delivery of such molecules to the early Earth may have played a role in the origin and evolution of life.

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are believed to be among the most widespread and abundant organic compounds in the universe (Allamandola et al. 1999; Cox and Kessler 1999). These compounds are a ubiquitous component of the organic carbon in meteorites and interplanetary dust particles (IDPs) (see Ehrenfreund and Charnley [2000] for a review). In addition, infrared features generally attributed to PAHs (the so-called “unidentified infrared bands”) have been observed in the gas phase in a wide range of extraterrestrial environments, including protoplanetary and planetary nebulae, reflection nebulae, HII regions, the diffuse interstellar medium, and in lines of sight through dense molecular clouds (Sellgren et al. 1995; Boulanger et al. 1998; Allamandola et al. 1999; Brooke et al. 1999; Bregman et al. 2000; Chiar et al. 2000; Bregman and Temi 2001).

One reason for the abundance and ubiquity of PAHs in extraterrestrial environments is the stability of their aromatic structures. Aromaticity is not limited to species containing only carbon and hydrogen. Nitrogen, the fourth most abundant reactive interstellar element, can also be incorporated into aromatic compounds. Interstellar PAHs are thought to form predominantly in the circumstellar shells and outflows of carbon-rich, late-type giants by repeated hydrogen abstraction and addition of acetylene ( $C_2H_2$ ) molecules to form rings (Allamandola et al. 1989; Wang and Frenklach 1994). Computational studies have shown that nitrogen can be incorporated into a PAH molecule by the replacement of a  $C_2H_2$  feedstock molecule with an HCN molecule (Ricca et al. 2001a; Ricca et al. 2001b). This substitution may lead to the formation of a polycyclic aromatic nitrogen heterocycle (PANH). Although PANHs are subject to photodestruction, evidence suggests that they may

be protected in dense cloud environments (Peeters et al. 2005). Recent studies suggest that larger PANHs with one or more nitrogen atoms in the interior of the molecular skeleton could account for the 6.2  $\mu\text{m}$  interstellar emission band, and that such molecules may contain at least 1–2% of all cosmic nitrogen (Hudgins et al. 2005). In addition, PANHs such as purines, pyrimidines, quinolines, isoquinolines, and pyridines have been identified in carbonaceous chondrite meteorites at levels greater than 1 ppm, providing more evidence for the existence of extraterrestrial PANHs (see Sephton 2002 for a review). It is thus a reasonable assumption that PANHs comprise some portion of interstellar organic compounds.

In dense molecular clouds where temperatures are low (10–20 K), PAHs, PANHs, and other chemical species are expected to form mixed molecular ice mantles that are condensed on silicate dust grains (Sellgren et al. 1995; Sandford 1996; Chiar et al. 2000). These icy mantles, which are usually dominated by water ice, may then be subjected to chemical processing driven by ultraviolet radiation (either from the galactic background, embedded protostars, or cosmic-ray excitation of hydrogen) (Prasad and Tarafdar 1983; Bernstein et al. 1995; Cecchi-Pestellini et al. 2005) and/or by the impact of low-energy ( $\sim 1$  MeV) cosmic rays (Strazzulla 1997). The chemical processing of certain PAHs in laboratory analogs of these ices has been studied and a rich chemistry has been observed in which PAHs acquire a variety of side groups including hydroxy, carbonyl, methyl, and amino moieties (Bernstein et al. 2002; Bernstein et al. 2003).

Although the spectroscopic properties of PANHs have been studied (Mattioda et al. 2003; Bernstein et al. 2005; Hudgins et al. 2005), there has been no investigation of the compounds that are produced when PANHs undergo chemical processing in icy interstellar environments. The possibility that various side groups may be added to PANHs through interstellar ice processing is of interest for several reasons. First, as mentioned above, PANHs have been detected in carbonaceous chondrites. The detected compounds include PANHs with side groups, such as alkylated quinolines, isoquinolines, and pyridines (Hayatsu et al. 1975; Stoks and Schwartz 1982), and oxidized PANHs such as carboxylated pyridines and hydroxy- and keto-containing purines (xanthine, hypoxanthine, guanine, adenine) (Van der Velden and Schwartz 1977; Stoks and Schwartz 1981a, 1981b). Quinoline-quinones, another form of oxidized PANH, have also been tentatively identified in preliminary analysis of interstellar dust particles captured by the Stardust spacecraft (Krueger et al. 2003). Previous studies have investigated the connection between interstellar ice chemistry and meteoritic organics, pointing out that deuterium enrichments that are observed in meteorites suggest an interstellar origin for some meteoritic organics and that these deuterated excesses may be created in interstellar ice processing (Kerridge et al. 1987; Messenger et al. 1995; Sandford et al. 2000; Messenger 2002; Butterworth et al. 2004; Huang et al. 2005; Pizzarello and Huang 2005).

Another point of interest in the possible interstellar processing of PANHs is that substituted PANHs play an important role in biochemistry on Earth. The nucleobases found in DNA and RNA consist of substituted purines and pyrimidines, while other substituted PANHs such as flavins are involved in electron transfer processes. The possible interstellar formation of such compounds therefore has relevance to astrobiology.

In the work presented here, we report on the photochemical processing of the PANH quinoline in  $\text{H}_2\text{O}$ -dominated interstellar ice analogs. Quinoline was chosen as a nitrogen-containing analog of the PAH naphthalene, which was previously studied in similar investigations in this laboratory (Bernstein et al. 2001). A number of variables, including deposition temperature, UV flux, and ice composition, were explored in these experiments in order to simulate a variety of extraterrestrial environments.

## EXPERIMENTAL TECHNIQUE

The quinoline-containing interstellar ice analogs were prepared in a manner that has been described in detail elsewhere (Allamandola et al. 1988; Bernstein et al. 1995). In brief, a gas mixture is deposited onto a rotatable cold finger contained in an evacuated cryogenic chamber surrounded by an infrared spectrometer. The gas mixtures were prepared with quinoline (98%, Sigma-Aldrich, distilled prior to use), water (purified via a Millipore Milli-Q system to 18.2 M), methanol (HPLC grade, Fisher), and methane (ultra-high purity, Matheson). The quinoline, water, and methanol were triply freeze-pump-thawed to remove dissolved gases. Pure  $\text{H}_2\text{O}$  deposited under these conditions is in its high-density amorphous form when deposited at 15 K and goes through several phase transitions during warming (Jenniskens and Blake 1994; Jenniskens et al. 1995). Clearly, the morphology of ice mixtures can be more complex, but previous IR spectra of  $\text{H}_2\text{O}$ :quinoline mixtures are consistent with amorphous  $\text{H}_2\text{O}$  (Bernstein et al. 2005). This form is believed to be representative of  $\text{H}_2\text{O}$ -rich ices in interstellar molecular clouds.

For the work described here, gas mixtures typically contained  $<1$  mbar of  $\text{H}_2\text{O}$  and quinoline at a ratio of 50:1 and were deposited onto a 20 K aluminum foil substrate for  $\sim 6$  hr at an ice growth deposition rate of  $\sim 0.7$   $\mu\text{m/hr}$ . Residual pressure in the vacuum chamber was  $\sim 5 \times 10^{-8}$  bar. Several variations on this typical preparation were also used to assess the effects of different parameters on ice photochemistry. These variations included the following:

1. Using a CsI substrate instead of aluminum foil in order to take infrared spectra
2. Slowing the rate of ice growth deposition to  $\sim 0.07$   $\mu\text{m/hr}$  to increase UV dose while depositing for 48 hr
3. Changing the  $\text{H}_2\text{O}$ :quinoline ratio to 10:1 and 100:1
4. Including  $\text{CH}_4$  or  $\text{CH}_3\text{OH}$  vapor at levels  $\sim 10\%$  of the  $\text{H}_2\text{O}$

5. Changing the deposition temperature to 122 K to simulate outer solar system, rather than interstellar, conditions
6. Simultaneously depositing water and quinoline vapors from separate borosilicate tubes for 48 hr in order to increase the yield of material for analysis

Ultraviolet photolysis occurred simultaneously with vapor deposition; photolysis was provided by a microwave-powered, flowing-hydrogen discharge lamp (Warneck 1962) that produces an output nearly evenly divided between the Lyman  $\alpha$  line and a 20 nm wide molecular transition centered at 160 nm. The lamp was operated at  $\sim 100$  mbar of pressure for the  $H_2$  gas and with microwave settings of 70% forward power and 6% reflected power. The flux of such lamps has been shown to vary with time and operating conditions, but in this work, we have assumed a nominal flux of  $\sim 2 \times 10^{15}$  photons  $cm^{-2} s^{-1}$  (Warneck 1962; Cottin et al. 2003; Loeffler et al. 2005). Based on the absorption cross-section of water ice, it has been estimated that 90% of the flux from this type of UV irradiation is absorbed within the first 0.1  $\mu m$  of a pure water ice (Cottin et al. 2003). Given this optical depth, the molecules in the ices deposited at 0.7  $\mu m/hr$  would have experienced  $\sim 8.5$  min of radiation ( $\sim 1 \times 10^{18}$  photons  $cm^{-2}$ ). The molecules in the ices deposited at 0.07  $\mu m/hr$  would have experienced more photolysis ( $\sim 85$  min) prior to shielding by ice layers and were used to assess the effects of UV flux on product distribution and yield.

After deposition and photolysis, the ices were warmed to 220 K at 2 K/min under dynamic vacuum. The foil substrate containing the sample was then removed from the system and quickly placed in a glass vial containing 500  $\mu L$  of HPLC-grade methanol (Fisher) and sonicated to dissolve the ice residue. This methanol extract was then analyzed by the methods described below. For the ices on CsI substrates, infrared spectra were measured both before and after warm-up. High-performance liquid chromatography (HPLC) was used to separate and analyze aliquots of the methanol extracts. HPLC was performed on a 5  $\mu L$  sample injection with a Hewlett-Packard 1100 series HPLC equipped with both a diode array UV/VIS detector and a fluorescence detector. The separation utilized a Vydac 218TP54 column ( $4.6 \times 250$  mm, 5  $\mu m$ , C18) and a mobile phase gradient beginning with 30% A (methanol) and 70% B (pH 5.5 50 mM sodium acetate + 8% methanol) changing to 56.7% A and 43.3% B over 40 min at 0.5 mL/min. The absorbance at 230 nm was monitored to measure elution of peaks. The HPLC grade methanol, sodium hydroxide, and acetic acid for the HPLC buffer were all obtained from Fisher.

Peaks were identified by comparison of retention time and UV spectrum with those of a given standard. Standards were purchased from Sigma-Aldrich and included the following compounds: 2-hydroxyquinoline; 4-hydroxyquinoline; 5-hydroxyquinoline; 6-hydroxyquinoline; 7-hydroxyquinoline; 8-hydroxyquinoline; quinoline N oxide; 2,4-dihydroxyquinoline; 2,6-dihydroxyquinoline; and 2,8-

dihydroxyquinoline. Abundances were estimated by comparing peak areas to a linear fit through zero of the standard at five different concentrations. Unfortunately, 2-hydroxyquinoline and 5-hydroxyquinoline co-eluted under the conditions used, so it was impossible to determine abundances for these compounds. The possible presence of two other hydroxyquinolines could not be assessed in this study; 8-hydroxyquinoline was not detectable by our methods (Nagiel-Ostaszewski et al. 1991), and 3-hydroxyquinoline could not be purchased for comparison.

The methanol extracts of the ice residues were also separated by nanoscale liquid chromatography (nanoLC) performed using a photopolymerized sol-gel (PSG) monolithic stationary phase and analyzed by electrospray ionization-mass spectrometry (ESI-MS). The ability to inject long sample plugs on the PSG columns without losing chromatographic resolution (preconcentration) enhances the detection sensitivity for this scheme (Quirino et al. 2001). Preparation of 30 cm long pentafluorophenyl-derivatized PSG monolith capillary columns is described elsewhere (Dulay et al. 2001) with the modification that 75  $\mu m$  i.d. fused-silica capillary columns with UV-transparent coating (purchased from Polymicro Technologies, Phoenix, Arizona, USA) were used. Methanol extracts were pressure-injected at 9 psi onto the column. Injection time was optimized for each sample and ranged from 60 s up to 12 hr. NanoLC was performed on an Eksigent NanoLC-1D system at a flow rate of 300  $\mu L/min$ . The mobile phase was a binary mixture consisting of 40% acetonitrile in a 5% solution of acetic acid in water. ESI-MS was performed on a Finnigan SSQ 700 quadrupole mass spectrometer (Finnigan MAT, San Jose, CA) equipped with an electrospray ion source. In this technique, analyte ions are ionized directly from the liquid phase, resulting in minimal fragmentation. Sheathless electrospray was performed by holding the electrospray tip voltage at 3 kV by an independent power supply. The quadrupole was scanned from  $m/z$  10 to 300 at 2.0 scan/s.

## RESULTS

### $H_2O$ :Quinoline Ices

Our analyses indicate that the UV photolysis of  $H_2O$ :quinoline ices produces a mixture of unreacted quinoline and a variety of hydroxyquinoline compounds formed by the substitution of hydroxy (-OH) groups for hydrogen atoms on the quinoline structure (Reaction 1).

The product composition was largely unaffected by changes in concentration, deposition temperature, or UV flux. Figure 1 presents an HPLC trace from the separation of the material resulting from photolysis of a  $H_2O$ :quinoline = 50:1 mixture at 20 K under the typical UV flux conditions described above, as well as traces from two control experiments. The irradiated  $H_2O$ :quinoline ice clearly shows a large peak caused by unreacted quinoline and smaller peaks

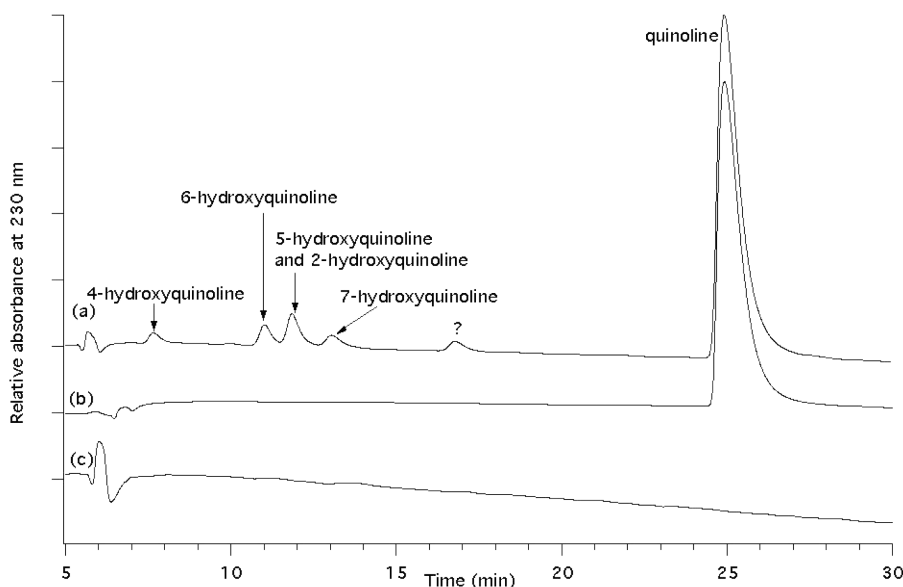
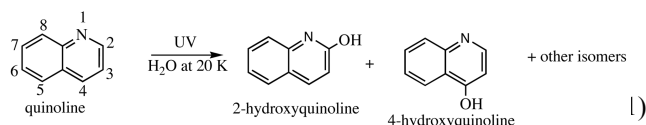
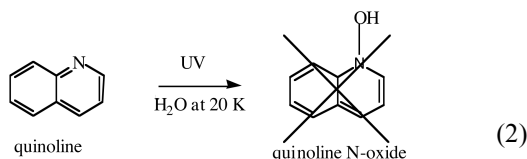


Fig. 1. An HPLC trace of the methanol extracts of the residues from (a) a  $\text{H}_2\text{O}$ :quinoline = 50:1 photolyzed ice, (b) an unphotolyzed  $\text{H}_2\text{O}$ :quinoline = 50:1 ice, and (c) a photolyzed  $\text{H}_2\text{O}$  ice (no quinoline). Hydroxyquinolines are produced on photolysis of the  $\text{H}_2\text{O}$ :quinoline ice, but not in the two controls. Peaks were identified by their elution time and UV spectrum.



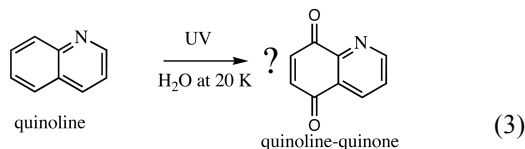
identified as 4-hydroxyquinoline, 6-hydroxyquinoline, the co-elution of 5-hydroxyquinoline and 2-hydroxyquinoline, and 7-hydroxyquinoline. No peaks matching the quinoline N oxide or the dihydroxyquinoline standards were observed (Reaction 2).



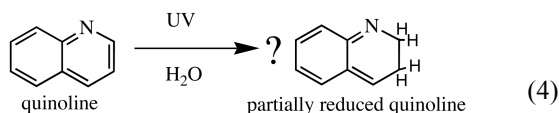
We were unable to identify the peak at 16.8 min, since we could not obtain standard samples of all the possible oxidized and reduced quinoline derivatives. It is reasonable to speculate that this peak could result from 3-hydroxyquinoline, a quinoline ketone or quinone, or a dihydroxyquinoline not searched for in this work. Control experiments carried out in the absence of either quinoline or UV radiation showed no evidence of hydroxyquinolines (Fig. 1). These experiments indicate that the hydroxyquinolines are not the result of contamination or non-photolytic reaction processes.

NanoLC-ESI-MS analysis (Fig. 2) of the methanol extract from the  $\text{H}_2\text{O}$ :quinoline = 50:1 ice supported the HPLC data. This analysis clearly showed the presence of unreacted

quinoline as well as multiple peaks with mass 145 amu, which correspond to the addition of an oxygen atom to the quinoline (most likely through the substitution of an alcohol group for a hydrogen atom, forming the hydroxyquinoline isomers seen in the HPLC data). In addition, the nanoLC-ESI-MS analyses of an ice created by a 48 hr long deposition (not shown) showed peaks at 159 amu, indicating the formation of a quinoline diketone, possibly quinoline-quinone (Reaction 3). This would be analogous to the photochemistry observed of naphthalene in  $\text{H}_2\text{O}$  ices (Bernstein et al. 2001). We also observed small peaks at 161 amu (possible dihydroxyquinolines; see trace (f) in Fig. 2).



Species with mass 131 amu and 133 amu were also observed (see traces (d) and (e) in Figure 2), which could be formed by partial reduction of the quinoline skeleton, although these were minor species compared to the oxidation products (Reaction 4). Reduction of this sort was observed in the photolysis of PAHs in  $\text{H}_2\text{O}$ -rich ices (Bernstein et al. 1999; Bernstein et al. 2002).



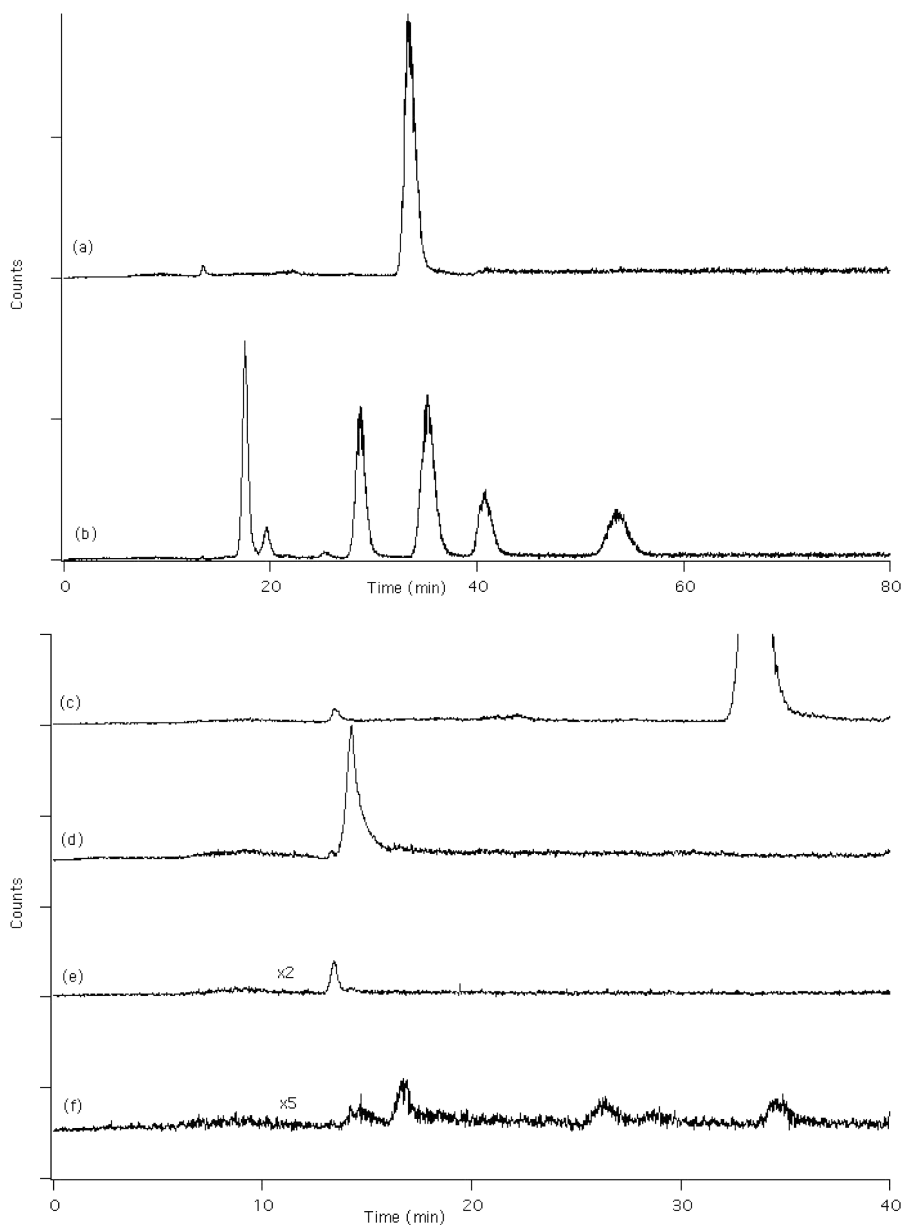


Fig. 2. NanoLC-ESI-MS chromatograms of the methanol extracts of the residue from a  $\text{H}_2\text{O}$ :quinoline = 50:1 photolyzed ice. The top box shows species with mass (a) 129 amu, corresponding to unreacted quinoline and (b) 145 amu, corresponding to hydroxyquinolines. The bottom box shows a magnified portion of the chromatograms for the following masses: c) 129 amu (unreacted quinoline), d) 131 amu (possibly partially reduced quinoline), e) 133 amu (possibly partially reduced quinoline), and f) 161 amu (possibly dihydroxyquinolines).

A comparison of the infrared spectra taken of  $\text{H}_2\text{O}$ :quinoline = 50:1 ices deposited with and without UV photolysis (Fig. 3) was consistent with the formation of an aromatic ketone, but was not definitive. This observation would be consistent with the interpretation of the nanoLC-ESI-MS peak at 159 amu as a diketone, or might suggest that some of the hydroxyquinolines reported above may be in equilibrium with the keto form, with the exact ratio of alcohol to ketone unknown. Again, keto-enol tautomerism is thought to play a similar role in the photolysis of PAHs in  $\text{H}_2\text{O}$ -rich ices (Bernstein et al. 1999).

We calculated the yields for the 4-hydroxyquinoline, 6-hydroxyquinoline, and 7-hydroxyquinoline products. In the typical experiments described above (UV flux =  $\sim 10^{18}$  photons  $\text{cm}^{-2}$ ), these yields were approximately 1.2%, 3.7%, and 4.8%, respectively, relative to unreacted quinoline. For comparison, we examined the HPLC traces of the methanol extracts from ices formed with the “slow” deposition rate (UV flux =  $\sim 10^{19}$  photons  $\text{cm}^{-2}$ ). The increase in UV flux yielded the same qualitative mix of compounds as the lower flux/higher deposition rate, but the overall yield of products relative to unreacted quinoline increased to approximately

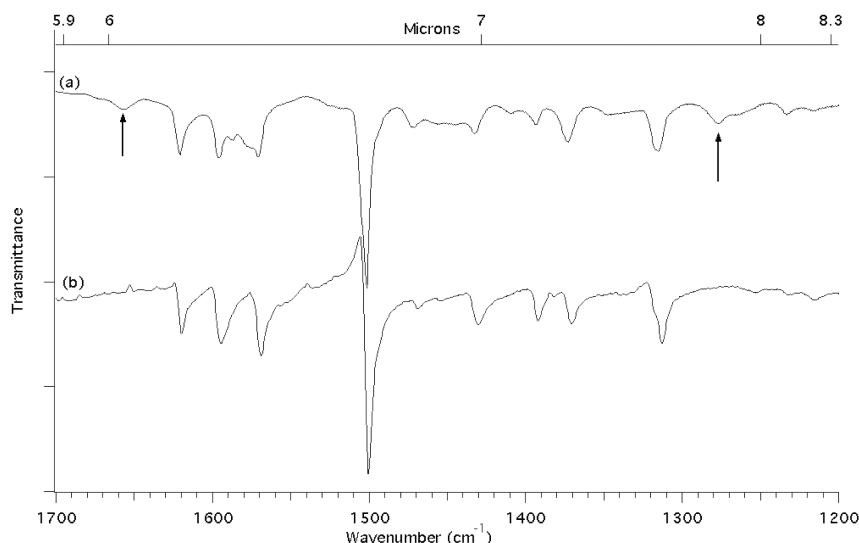


Fig. 3. Infrared (IR) spectra of (a) photolyzed  $\text{H}_2\text{O}$ :quinoline = 50:1 ice and (b) unphotolyzed  $\text{H}_2\text{O}$ :quinoline = 50:1 ice. Ices were formed at 20 K then warmed to 220 K for IR spectroscopy. Several changes are noticeable; the arrows in trace (a) point out the peaks at  $1657\text{ cm}^{-1}$  and  $1277\text{ cm}^{-1}$  that are suggestive of an aromatic ketone. Spectra were normalized to the height of the largest peak.

4.5%, 7.2%, and 11.5%, respectively. We found, however, that although the relative yields increased, the absolute yields (HPLC signal strength observed) of both the hydroxyquinolines and the unreacted quinoline decreased by approximately an order of magnitude, indicating a loss in the overall amount of quinoline and photoproducts.

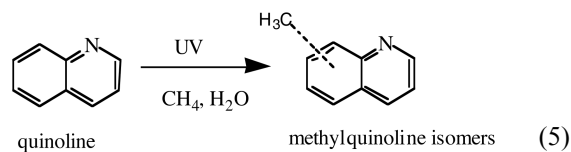
The UV photolysis of  $\text{H}_2\text{O}$ :quinoline = 10:1 and  $\text{H}_2\text{O}$ :quinoline = 100:1 mixtures showed qualitatively similar product distributions as the  $\text{H}_2\text{O}$ :quinoline = 50:1 mixture, with a range of hydroxyquinolines identified. Yields of 4-hydroxyquinoline and 7-hydroxyquinoline were slightly decreased for the 10:1  $\text{H}_2\text{O}$ :quinoline ice, but the yields for the 50:1 and 100:1 ices were comparable. Overall, the products observed are the same, and their relative proportions seem fairly insensitive to concentration.

### Ices Containing Methanol or Methane

Analysis of the methanol extracts from the ices containing methane or methanol revealed the addition of carbon atoms to the quinoline skeleton, as well as the previously observed oxygen atom addition. The HPLC trace of the  $\text{H}_2\text{O}$ : $\text{CH}_3\text{OH}$ :quinoline = 50:5:1 ice) (Fig. 4b) showed the same qualitative mix of hydroxyquinolines identified in the  $\text{H}_2\text{O}$ :quinoline = 50:1 ice (see Reaction 1 for structures and Fig. 4c for comparison). However, an additional peak at 22.1 min was also observed. This peak did not correspond to any of the methylquinoline standards or the 6-methoxyquinoline standard measured, but probably results from a methylquinoline or methoxyquinoline for which we did not have the standard. Yields for the hydroxyquinolines were much lower than those observed in the ices containing only  $\text{H}_2\text{O}$  and quinoline; 4-hydroxyquinoline was

undetectable while 6-hydroxyquinoline and 7-hydroxyquinoline produced yields of approximately 0.5% each relative to unreacted quinoline.

The nanoLC-ESI-MS analysis of the  $\text{H}_2\text{O}$ : $\text{CH}_3\text{OH}$ :quinoline ice revealed masses corresponding to unreacted quinoline (129 amu), methylquinolines (substituting a  $-\text{CH}_3$  group for a hydrogen atom; 143 amu), hydroxyquinolines (145 amu), and the possible simultaneous substitution of both a carbon-containing substituent (e.g., a methyl group) and an oxygen-containing substituent (e.g., a hydroxy group) (159 amu). Several methylquinoline isomers were thought to be present, but in the absence of relevant HPLC standards, the specific position of the methyl substituent could not be identified (see Reaction 5 for general structure).



The methylquinoline peaks were observed as minor products only; the preconcentration step in nanoLC-ESI-MS improves sample detection limits, which may explain the detection of methylquinolines by this method but not by the HPLC analysis. The peaks representing hydroxyquinolines and possible simultaneous substitution were quite large in comparison. The multiple species with mass 159 amu could be caused by substitution of a methyl group on to a hydroxyquinoline or by substitution of either a  $-\text{CH}_2\text{OH}$  or a  $-\text{OCH}_3$  group as a single moiety (Reaction 6). The 159 amu peaks could also indicate the presence of a diketone, as suggested in the  $\text{H}_2\text{O}$ :quinoline results; however, this

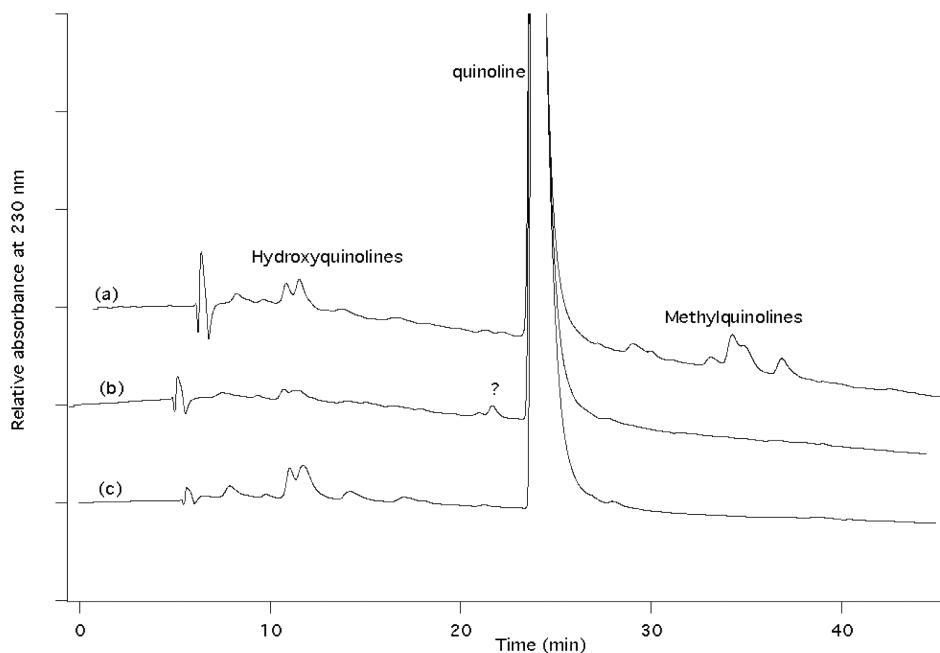
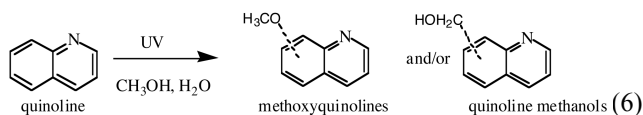


Fig. 4. HPLC traces of methanol extracts of residues from ices containing (a)  $\text{H}_2\text{O}:\text{CH}_4:\text{quinoline} = 50:5:1$ , (b)  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{quinoline} = 50:5:1$ , and (c)  $\text{H}_2\text{O}:\text{quinoline} = 50:1$ . Regions with peaks corresponding to hydroxyquinolines, unknown species, unreacted quinoline, and methylquinolines are indicated.

assignment seems less likely because the potential diketone was only weakly observed in the  $\text{H}_2\text{O}:\text{quinoline}$  ice after a much longer deposit.

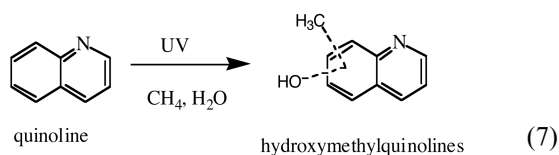


Photolysis of a  $\text{H}_2\text{O}:\text{CH}_4:\text{quinoline} = 50:5:1$  ice again produced the hydroxyquinolines described above, but HPLC analysis of this mixture also indicated the presence of methylquinoline compounds (Fig. 4a). The peak at 32.4 min is tentatively identified as 8-methylquinoline, while the other peaks in the range of 33–37 min are likely to be other methylquinolines. It is difficult to assign exact identifications both because of the limited supply of methylquinoline standards and because of the similarity in the retention times and UV spectra of these compounds. Yields for the hydroxyquinolines produced in this ice were  $\sim 0.75\%$ ,  $1.6\%$ , and  $1.8\%$  for 4-, 6-, and 7-hydroxyquinoline relative to unreacted quinoline. The peak identified as 8-methylquinoline was produced with a yield of approximately  $1.3\%$  relative to unreacted quinoline.

NanoLC-ESI-MS analysis of the extract from the  $\text{H}_2\text{O}:\text{CH}_4:\text{quinoline} = 50:5:1$  ice revealed species with masses similar to those observed in the  $\text{CH}_3\text{OH}$ -containing ice. Again, methylquinolines (143 amu) and hydroxyquinolines (145 amu) were observed, consistent with the HPLC analysis. Several peaks at 159 amu corresponding to species arising

from possible simultaneous substitution of carbon- and oxygen-containing groups were also present.

A comparison of the chromatograms for the 159 amu mass between the  $\text{CH}_3\text{OH}$ -containing ice and the  $\text{CH}_4$ -containing ice reveals differences in the distribution of species formed by possible simultaneous addition of carbon- and oxygen-containing moieties (Fig. 5). In the  $\text{CH}_3\text{OH}$ -containing ice, there appears to be one major species and one minor species, while the  $\text{CH}_4$ -containing ice contains several species of similar prominence. It is reasonable to suggest that the products in the  $\text{CH}_3\text{OH}$ -containing ice result from the addition of one single moiety, either as the  $-\text{CH}_2\text{OH}$  alcohol or the  $-\text{OCH}_3$  methyl ether (Reaction 6). This is consistent with previous analyses of ices containing PAHs and  $\text{CH}_3\text{OH}$ , where formation of the methyl ether of the PAH was observed (Bernstein et al. 2002). In the  $\text{CH}_4$ -containing ice, however, it is possible that the 159 amu species are the result of the addition of separate  $-\text{CH}_3$  groups and  $-\text{OH}$  groups, producing several isomers of methylhydroxyquinoline (Reaction 7).



We examined the effects of deposition temperature on photolysis in the  $\text{H}_2\text{O}$ - and  $\text{CH}_4$ -containing ices. A change in deposition temperature from 20 K to 122 K did not affect the

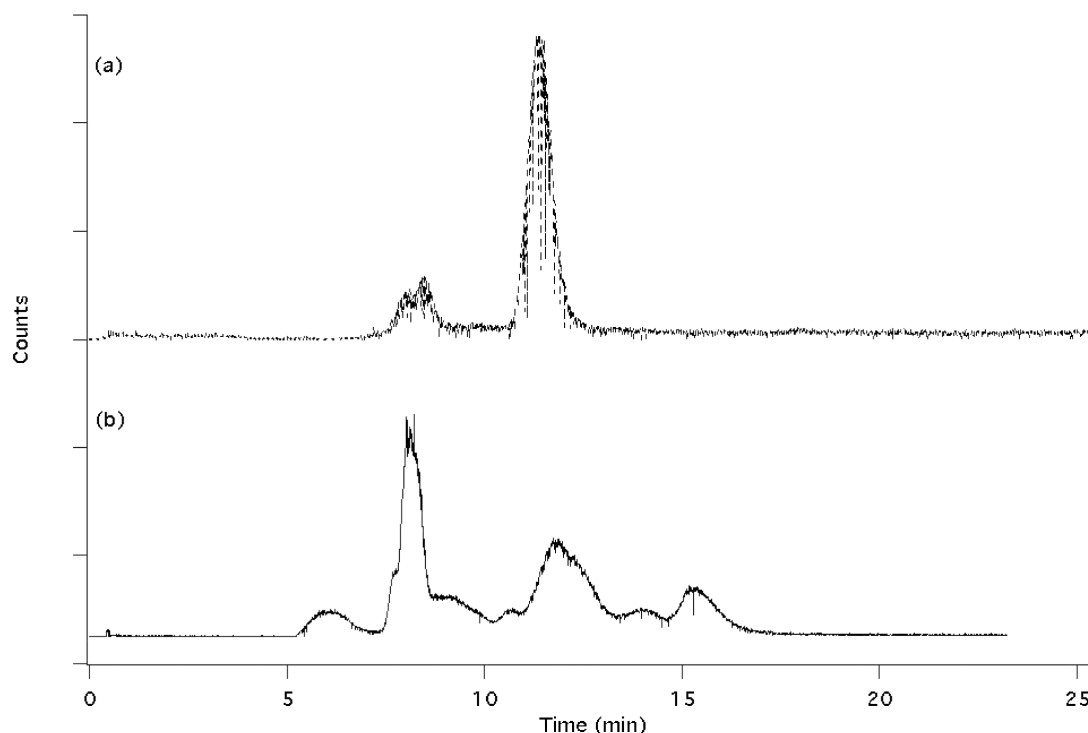


Fig. 5. NanoLC-MS-ESI chromatograms for species with a mass of 159 amu in the methanol extracts of the residue of (a)  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{quinoline} = 50:5:1$  ice and (b)  $\text{H}_2\text{O}:\text{CH}_4:\text{quinoline} = 50:5:1$  ice. A single large peak dominates the former, consistent with the substitution of  $\text{CH}_3\text{OH}$  as a single moiety ( $-\text{OCH}_3$  or  $-\text{CH}_2\text{OH}$ ), while the multiple peaks in trace (b) suggest substitution of two separate groups ( $-\text{CH}_3$  plus  $-\text{OH}$ ).

range of hydroxyquinolines produced in the  $\text{H}_2\text{O}:\text{quinoline} = 50:1$  ice, although the overall yield of the products relative to unreacted quinoline dropped. When the  $\text{H}_2\text{O}:\text{CH}_4:\text{quinoline} = 50:5:1$  ice was deposited and photolyzed at 122 K, however, methylquinolines were not observed in the HPLC analysis of the product mixture, although hydroxyquinolines were still detected. This lack of methylquinoline formation is most likely because the volatile methane did not freeze efficiently into the ices at this temperature.

## DISCUSSION

We have subjected quinoline-containing interstellar ice analogs to UV photolysis and then analyzed the resulting photoproducts. We demonstrate that substituted quinolines are readily produced under astrophysically relevant conditions. Specifically, hydroxyquinolines are formed in quinoline-containing  $\text{H}_2\text{O}$  ices under a range of conditions, which mirrors the results observed from photolysis of PAHs in  $\text{H}_2\text{O}$  ice (Bernstein et al. 2001). This result suggests that oxidation of aromatics in water-rich icy environments is a facile and favorable reaction. Our observations correlate well with the tentative, preliminary identification of quinoline-quinones in apparently interstellar dust particles detected by the Stardust spacecraft (Krueger et al. 2003). Although we could not confirm the presence of these quinones directly in

our laboratory analogs (and standards were not available for comparison), we did see species with the appropriate mass (159 amu) produced in a long-term ice deposit. Their formation is also a logical extension of the formation of the oxidized quinolines that we could confirm.

We also observed products resulting from the possible addition of hydrogen to the quinoline structure, indicating that PANHs might also be reduced in these environments. Nevertheless, reduction products were of low abundance compared to oxidation products. Again, these observations correlate well with previous studies of PAHs (Bernstein et al. 1999).

Our results also indicate that in environments with a high UV flux, photodestruction of quinoline may compete with the oxidation reaction. This observation is in agreement with recent studies that indicate that although small PANHs are not expected to survive the radiation environment in the diffuse interstellar medium, they could survive within a dense cloud (Peeters et al. 2005). The UV flux within a dense molecular cloud has been estimated in various literature reports as  $1.4 \times 10^3 \text{ photons cm}^{-2} \text{ s}^{-1}$  or  $4.8 \times 10^3 \text{ photons cm}^{-2} \text{ s}^{-1}$  (Prasad and Tarafdar 1983; Menella et al. 2003). At the edge of such a cloud, the flux can be approximated as  $\sim 10^8 \text{ photons cm}^{-2} \text{ s}^{-1}$  (Mathis et al. 1983). Given this range, our typical UV dose corresponds to approximately  $6 \times 10^6$ – $2 \times 10^7 \text{ yr}$  in the interior of a dense cloud (a reasonable time scale representing the



lifetime of the cloud) or  $\sim 500$  yr at the edge of the cloud. The experiments done at slower deposition rate would receive approximately an order of magnitude more UV exposure; these are the experiments that showed evidence of photodestruction of quinoline. Thus, the production of significant amounts of oxidized PANHs may be limited to the interior of dense clouds, where shielding protects the compounds from complete photodestruction but sufficient amounts of UV are present to drive the photooxidation reactions.

The observations related to the oxidation of PANHs are insensitive to concentration or temperature. Thus, we expect that if PANHs were delivered to planetary icy surfaces, they would undergo oxidation in those environments as well. We observed formation of hydroxyquinolines at temperatures of  $\sim 120$  K, an appropriate temperature for modeling outer solar system bodies such as Europa (Spencer et al. 1999). If PANHs are present on such bodies, it is likely that a significant fraction will be oxidized through photochemistry in  $\text{H}_2\text{O}$ -dominated ices.

Previous studies of the photochemistry of PAHs focused on coronene ( $\text{C}_{24}\text{H}_{12}$ ), a highly symmetric molecule that has only one possible mono-alcohol or mono-ketone, and naphthalene ( $\text{C}_{10}\text{H}_8$ ), a structure with two possible mono-alcohols. In contrast, the regiochemistry of quinoline is far more complex, with eight possible distinct oxygen substitution sites (including the nitrogen oxide). Our results did not show a clear dominance of any single site; a mixture of at least five monohydroxyquinolines was observed, with the 7-hydroxyquinoline having a slightly higher yield than the other products. Quinoline N oxide was not observed, suggesting that oxidation is much more likely to occur at the carbon atoms than the lone nitrogen atom.

We also observed the substitution of methyl and methoxy moieties on to the quinoline skeleton when  $\text{CH}_4$  or  $\text{CH}_3\text{OH}$  was present in the interstellar ice analogs. The methane or methanol was present at levels  $\sim 10\%$  that of the  $\text{H}_2\text{O}$  in the ice. The observed abundance ratio for  $\text{CH}_3\text{OH}$  along most lines of sight in interstellar dense clouds is  $\sim 10\%$ , although this may be an average value caused by two distinct icy grain mantle populations (one methanol-rich and the other methanol-poor) (Skinner et al. 1992; Dartois et al. 1999). We view the levels used in our experiments as a representative concentration for methanol in interstellar dense clouds (Chiar et al. 1996; Pontopiddan et al. 2003), and a slightly high, but experimentally expedient, approximation for methane (Lacy et al. 1991; Boogert et al. 1996). This formation of methylquinolines and possible methoxyquinolines or methylhydroxyquinolines in our experiments parallels results observed in photolysis of PAHs in interstellar ice analogs (Bernstein et al. 2002). The formation of methylquinolines is of particular interest to meteoritics. Substituted quinolines with up to four methyl side groups have been identified in the Murchison meteorite (Stoks and Schwartz 1982). Previous studies based on deuterium enrichments suggest a connection

between interstellar ice chemistry and meteoritic organics (Kerridge et al. 1987; Messenger et al. 1995; Sandford et al. 2000; Messenger 2002). The formation in our ice experiments of methylquinolines similar to those observed in Murchison lends support to this proposed connection.

If these ice reactions of quinoline are linked to the production of meteoritic organic material, then a portion of the meteoritic aromatic compounds would be expected to be oxidized. Although PANHs have been identified in the Murchison meteorite, there have been very few studies focusing on meteoritic PANHs, and almost no attention has been paid to the possibility of oxidized PANHs in meteorites. In fact, there has been relatively little study of any oxidized aromatics in meteorites, although a number of aromatic ketones (e.g., fluorenone, anthracenone, anthracenedione, benzoanthracenone) have been identified (Basile et al. 1984; Krishnamurthy et al. 1992). Targeted searches for PANHs and their oxidized and reduced derivatives are needed to determine if these compounds are present in meteorites. There are certainly several possible pathways to the formation of meteoritic organics, and chemistry in icy environments is only one proposed method. Because oxidized PANHs are the most abundant products observed in our work, information on the relative prevalence of oxidation in PANH meteoritic compounds could provide insight into the possible significance of ice chemistry in the formation of meteoritic organics.

In addition, PANHs are of significant astrobiological interest. Purine- and pyrimidine-based nucleobases, which make up the information component of DNA and RNA, are essentially PANHs with side groups including hydroxy and methyl moieties. Other important biomolecules, including two amino acids, flavins, and nicotinamides, are built on PANH skeletons modified with side groups. If the simple PANH skeletons such as purine and pyrimidine are present in the interstellar medium or on icy planetary surfaces, then the ice chemistry described here could provide one facile method for attaching the side groups and making putatively prebiologically relevant molecules (e.g., hypoxanthine or xanthine, both formed by substitution of hydroxy groups for hydrogen atoms on purine and both playing roles in modern biological processes). This possibility is potentially important both as a means of contributing these compounds to prebiotic environments where they may play a role in the origination of life, and because these molecules could act as false biomarkers, confusing the search for compounds that could indicate life elsewhere in the galaxy.

## CONCLUSIONS

We have shown that the polycyclic aromatic nitrogen heterocycle quinoline is readily oxidized by UV photolysis when frozen in astrophysically relevant  $\text{H}_2\text{O}$ -dominated ices. A variety of hydroxyquinolines is produced, with no single dominant product. Quinoline N oxide was not formed.

Oxidation occurs at temperatures relevant to dense molecular clouds and to icy planetary surfaces and is qualitatively unaffected by quinoline concentration. Reduction is also consistent with these observations. UV doses comparable to those expected in the interior of a dense molecular cloud over its lifetime ( $\sim 10^{18}$  photons  $\text{cm}^{-2}$ ) produce significant levels of oxidation without large amounts of photodestruction of the resulting photoproducts, although an increase in UV exposure by a factor of 10 appears to cause photodestruction of quinoline.

We have also shown that side groups such as methyl and methoxy moieties may be added to the quinoline skeleton when methane or methanol is present in these ices at appropriate levels. The methylquinolines formed are similar to compounds detected in the Murchison meteorite. The formation of these compounds is of interest because it may provide insight into the connection between interstellar ice chemistry and meteoritic organics. For example, given that methylquinolines have previously been detected in the Murchison meteorite, our current results lead us to suspect the presence of hydroxyquinolines as well. Future targeted searches for oxidized aromatics in meteorites should provide information on this possibility. In addition, the astrobiological relevance of PANHs and their substituted derivatives presents intriguing reasons to study further the formation and reactions of these compounds.

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